

Serial Number:  
Applicants: Bayya et al

Patent Application  
Navy Case Number: 84,936

What is claimed:

1. A process for preparing a BGG glass material comprising the steps of

(a) melting BGG glass components at a melting temperature comprising barium oxide (BaO) and/or barium carbonate ( $\text{BaCO}_3$ ), gallium oxide ( $\text{Ga}_2\text{O}_3$ ), germanium oxide ( $\text{GeO}_2$ ), or a precursor thereof, and a halogen component at a temperature above liquidus temperature of the BGG glass to form a BGG glass melt; amounts of the BGG glass components are in the BGG glass forming region;

(b) quickly cooling the BGG glass melt to avoid crystallization to below glass transition temperature of the BGG glass to form a BGG glass;

(c) annealing the BGG glass at a temperature above the glass transition temperature but below crystallization temperature; and

(d) slowly cooling the BGG glass after annealing to a temperature below the glass transition temperature to form the BGG glass material.

2. The process of claim 1 including the step of fining the BGG glass melt at about the glass melting temperature.

3. The process of claim 2 wherein the halogen component is selected from the group consisting of halogen gases, halide compounds and mixtures thereof.

4. The process of claim 3 wherein the melting temperature is about  $1300^\circ\text{C}$ , the liquidus temperature is about  $1150^\circ\text{C}$ , the crystallization temperature is about  $800^\circ\text{C}$ , and the glass transition temperature is about  $675^\circ\text{C}$ .

5. The process of claim 4 wherein the step of fining is conducted for a period of about one hour

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to remove bubbles from the glass melt and the glass melt is rapidly cooled from about the melting temperature to about the room temperature at which the BGG glass melt is in solid state and then heating the BGG glass from about room temperature to about 700°C for annealing for a period of several hours to remove at least some of the stresses caused by the rapid cooling step.

5 6. The process of claim 5 wherein the rapid cooling step is conducted at a rate on the order of about 50°C per minute and wherein the slow cooling step is conducted at a rate on the order of about 1°C per minute.

7. The process of claim 3 including the step of adding rubidium oxide ( $\text{Rb}_2\text{O}$ ) and/or cesium oxide ( $\text{Cs}_2\text{O}$ ) to the BGG glass components in order to introduce rubidium ions and/or cesium  
10 ions into the BGG glass material.

8. The process of claim 7 including the step of ion exchanging cesium ions for rubidium ions.

9. The process of claim 2 wherein the halogen component is selected from the group consisting of barium chloride ( $\text{BaCl}_2$ ), rubidium chloride ( $\text{RbCl}$ ), cesium chloride ( $\text{CsCl}$ ), and mixtures thereof.

15 10. The process of claim 2 wherein amount of germanium oxide is 35-90 mole %, amount of gallium oxide is 0.1-25 mole %, amount of barium oxide and/or barium carbonate is 0.1-50 mole %, and amount of the halogen component is 0.1-20 mole %, and wherein the BGG glass components include 0-50 mole % cesium oxide and 0-50 mole % rubidium oxide.

11. The process of claim 7 wherein amount of germanium oxide is 40-60 mole %, amount of  
20 gallium oxide is 10-18 mole %, amount of barium oxide and/or barium carbonate is 20-45 %, amount of cesium oxide is 0-40 mole %, amount of rubidium oxide is 0-40 mole %, and amount

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of the halogen component is 1-10 mole %.

12. The process of claim 11 wherein the halogen component is selected from the group consisting of barium chloride, rubidium chloride, cesium chloride and mixtures thereof.

13. The process of claim 3 including the step of adding seed material during the melting step to form crystals within the BGG glass material, nucleating the seed material at a nucleating temperature which is below the melting temperature and growing the crystals at a temperature above the nucleating temperature before the slow cooling step.

14. The process of claim 13 including the step of mixing the BGG glass components below the melting temperature.

15. The process of claim 13 wherein duration of said nucleating and said crystal growth steps is about one hour.

16. The process of claim 14 wherein duration of said nucleating and crystal growth steps is about one hour.

17. The process of claim 13 including the steps of cooling at a rate on the order of about 5°C per minute after said crystal growth step down to near the glass transition temperature, holding at about the glass transition temperature to equalize inside and outside temperature, then cooling at a rate on the order of about 1°C per minute.

18. A BGG glass material having less than 1 part per million hydroxyl ions made from, on mole percent basis:

(a) germanium oxide ( $\text{GeO}_2$ )	35-90
(b) gallium oxide ( $\text{Ga}_2\text{O}_3$ )	0.1-25

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|---|--------|
| (c) barium oxide ( $\text{BaO}$ ) and/or barium carbonate ( $\text{BaCO}_3$ ) | 0.1-50 |
| (d) cesium oxide ( $\text{Cs}_2\text{O}$ )                                    | 0-50   |
| (e) rubidium oxide ( $\text{Ru}_2\text{O}$ )                                  | 0-50   |
| (f) halogen component   | 0.1-20 |

5      19. A BGG glass material made from, on mole % basis:

- |   |       |
|---|-------|
| (a) germanium oxide ( $\text{GeO}_2$ )  | 40-60 |
| (b) gallium oxide ( $\text{Ga}_2\text{O}_3$ )                                 | 10-18 |
| (c) barium oxide ( $\text{BaO}$ ) and/or barium carbonate ( $\text{BaCO}_3$ ) | 20-45 |
| (d) cesium oxide ( $\text{Cs}_2\text{O}$ )                                    | 0-40  |
| 10      (e) rubidium oxide ( $\text{Ru}_2\text{O}$ )                          | 0-40  |
| (f) halogen component   | 1-10  |

20. The BGG glass material wherein said halogen component is selected from the group consisting of barium chloride, rubidium chloride, cesium chloride and mixtures thereof.